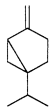
IUPAC Task Group on Atmospheric Chemical Kinetic Data Evaluation – Data Sheet NO3_VOC38

This data sheet last evaluated: June 2013; last change in preferred values: June 2013.



NO_3 + (sabinene) → products

Rate coefficient data

k/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Technique/ Comments
Absolute Rate Coefficients			
$(1.07 \pm 0.16) \times 10^{-11}$	298	Martínez et al., 1999	DF-LIF (a)
$2.3 \times 10^{-10} \exp[-(940 \pm 200)/T]$	298-393		
Relative Rate Coefficients			
$(1.01 \pm 0.03) \times 10^{-11}$	296	Atkinson et al., 1990	RR (b)
$(6.8 \pm 0.12) \times 10^{-12}$	296		RR (c)

Sabinene is 1-isopropyl-4-methylene-bicyclo[3.1.0]hexane.

Comments

(a) NO_3 radicals (6-30 × 10^{11} molecule cm^{-3}) generated from reaction of F atoms (made in a microwave discharge through F_2/He) with HNO_3. Flow tube was operated at ~1.33 mbar (1 Torr) He at 4 temperatures between 298 and 393 K. Sabinene was present at similar concentrations (1-3 fold) to NO_3. So that absolute NO_3 concentrations (derived by titration with tetramethylethene) were necessary to derive the rate coefficient.

(b) Relative rate of loss of sabinene and 2-methyl-2-butene (reference reactant) in a 6400 L Teflon chamber at 980 mbar (735 Torr) of air was monitored by GC. NO_3 was generated by the thermal decomposition of N_2O_5. The rate constant ratio, $k(NO_3$ + sabinene) / $k(NO_3$ + 2-methyl-2-butene) = 1.08 ± 0.03 is placed on an absolute basis using $k(NO_3$ + 2-methyl-2-butene) = 9.37 × 10^{-12} cm^3 molecule^{-1} s^{-1} at 298 K (Atkinson and Arey, 2003).

(c) Relative rate of loss of sabinene and trans-2-butene (reference reactant) in a 6400 L Teflon chamber at 980 mbar (735 Torr) of air was monitored by GC. NO_3 was generated by the thermal decomposition of N_2O_5. The rate constant ratio, $k(NO_3$ + sabinene) / $k(NO_3$ + trans-2-butene) = 1.74 ± 0.03 is placed on an absolute basis using $k(NO_3$ + trans-2-butene) = 3.9 × 10^{-13} cm^3 molecule^{-1} s^{-1} at 298 K (IUPAC 2013, datasheet NO_3_VOC30).

.

Preferred Values

Parameter	Value	T/K
k /cm^3 molecule^{-1} s^{-1}	1.0×10^{-11}	298
Reliability		
$\Delta \log k$	± 0.15	298

Comments on Preferred Values

The preferred value at 298 K is based on the absolute study of Martínez et al. (1999) and the relative rate study of Atkinson et al, using 2-methyl-2-butene as reference. These two rate coefficients are in good agreement, but are ≈ 30 % larger than that obtained using trans-2-butene as reference reactant. The error limits have been extended to reflect this. The significant, positive dependence of k on temperature observed by Martínez et al. (1999) requires validation.

There are no product studies of this reaction, though the large rate constant indicates that the reaction proceeds mainly via addition of NO_3 across a double bond to form a chemically activated nitrooxyalkyl radical. At pressures found in the troposphere this adduct will undergo collisional stabilization prior to reaction with O_2 to form a nitrooxyalkyl peroxy radical or decompose to release NO_2. At atmospheric pressure the formation of the peroxy radical will generally dominate.

References

Atkinson, R., Aschmann, S. M., and Arey, J., Atmos. Env. A, 24, 2647-2654, 1990

Atkinson, R.: J. Phys. Chem. Ref. Data, 26, 215-290, 1997.

Atkinson, R., and Arey, J., Chem. Rev., 103, 4605-4638, 2003.

Corchnoy, S. B., and Atkinson, R., Env. Sci. Tech., 24, 1497-1502, 1990.

IUPAC, Task Group on Atmospheric Chemical kinetic data evaluation. (Ammann, M., Atkinson, R., Cox, R.A., Crowley, J.N., Hynes, R. G., Jenkin, M.E., Mellouki, W., Rossi, M. J., Troe, J. and Wallington, T. J.) Evaluated kinetic data: http://iupac.pole-ether.fr, 2013.

Martínez, E., Cabañas, B., Aranda, A., Martín, P., and Salgado, S., J. Atmos. Chem., 33, 265-282, 1999.